

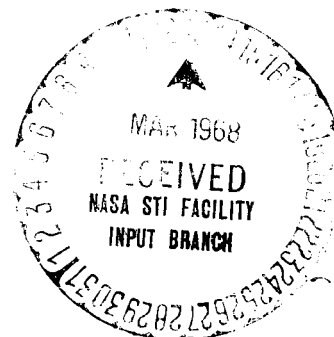
THE DIRECT ADSORPTION OF CO₂ BY QUICKLIME

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THE DIRECT ADSORPTION OF CO₂ BY QUICKLIME

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ABSTRACT. An analysis of the direct reaction between CaO and CO₂ gas to form CaCO₃ at 500-700°C was performed to explain the retention of CaCO₃ within lumps of limestone after calcining, and the readsorption of CO₂ by CaO upon cooling of the interior of the lumps. A higher volume of CO₂ was adsorbed by CaO which had been calcined at lower temperatures. Glazed quicklime had lower porosity and consequently lower adsorption.

1. Introduction

Any discussion of the carbonation of quicklime normally involves the CaO \rightarrow Ca(OH)₂ \rightarrow CaCO₃ reaction at normal temperature. The discussion which follows, however, concerns the direct reaction between CaO and CO₂ atmosphere at temperatures of 500-700°C which results in the formation of CaCO₃.

When limestone is calcined in a lime kiln (vertical kiln), the quicklime is moved to a cooling bed subsequent to the termination of the decomposition reaction. At this plant, it has been noted that two different phenomena occur when this is done. The first of these is when some CaCO₃ remains within the lumps. Even though the surface temperature may be below the required decomposition temperature, a slight reaction continues to take place within the lump which is caused by an accumulation of thermal energy. The CO₂ liberated by this reaction attempts to escape to the outside, although this is impossible because the surface of the lump has already cooled. The CO₂ is thus readsorbed by the CaO, creating the effect of only partial calcination [1]. The other phenomenon observed has been when there is an irregular distribution of temperature within the cooling bed. In these instances, although the peripheral temperatures are below decomposition temperature ranges, the temperature remains high in spots where sectional decomposition continues to take place. The CO₂ which is liberated is readsorbed on the surface of the limestone on the periphery of these spots where the decomposition reaction has already terminated.

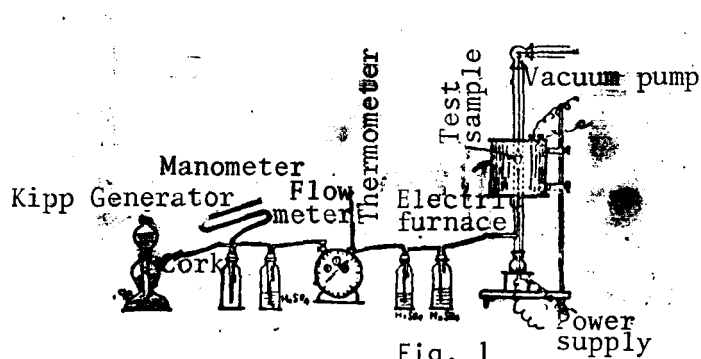
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Despite the fact that the central portions were thoroughly calcined and retained no CO_2 , some remained at the surface in the form of CaCO_3 . These phenomena have not been investigated, and things have been allowed to stand just as they were in the past. As the data obtained in the experiments which are described below demonstrate, it has been confirmed that CO_2 and CaO combine directly to form CaCO_3 in a CO_2 atmosphere at $500\text{--}700^\circ\text{C}$. It thus becomes possible to explain the above phenomena on the basis of these results.

The writer has previously reported on the microscopic examination of thin slices of limestone which had been calcined under different conditions than those described above. On the basis of measurements made of particle diameters, the data concerning the increases in particle size which accompany elevation in calcination temperature as well as the activity of quicklime in water were given [2]. It thus appeared possible that the measurement of CO_2 adsorption rates and quantities would provide a guide for estimating activity levels, particle size, and the temperature history of quicklime. Experiments were performed on the CO_2 adsorption of various types of quicklime prepared under constant calcining temperature conditions. The results are given below. The limestone used for these experiments, further, was fine crystalline limestone from Funajiri.

2. Optimum Carbonation Temperatures

Thermal weighing was used for the experiments in the carbonation of quicklime. A Kipp's generator, thermal scale, and vacuum pump were connected together as shown in Figure 1.



Equipment

When the CO_2 was passed through powdered calcined limestone, there was good initial contact between the CO_2 and the surface of the test sample. However, contact was generally poor between the CO_2 and the sample at the bottom of the dish, and for this reason, the adsorption throughout the material was not as had been expected. Consistent results could not be obtained for this reason. The size of the limestone particles was then changed to diameters on the order of 2 mm.

Initially, 1.5 g. of ground limestone was placed in a test dish. After thorough mixing with a mortar and pestle, it was heated to a temperature of 930°C at a heating rate of about 5°C/min. The CO₂ in the limestone samples should have been thoroughly discharged at this point; however, it was held at this temperature level for five minutes to provide a margin of safety. The electrical power supply was then cut off and the samples held "as is" until they had cooled to the desired temperature.

When the desired temperature level had been reached, CO₂ was passed through the material at a rate of 0.3-0.5 l/min from the gas generator. Concurrently, the electric current to the oven was turned on again and an effort was made to maintain constant temperature levels. During the course of this treatment, the weight of the sample of quicklime was measured. Seven different experimental temperature levels at 100°C intervals were established: 200,300,400,500, 600,700, and 800°C. The amount of weight increases is as given in Figure 2.

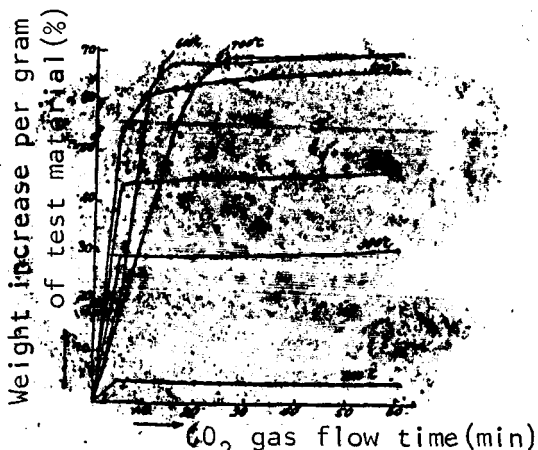


Fig. 2

CO₂ Absorption Rates of
Ground Quicklime
(Relationship to Atmospheric
Temperature)

Approximately maximum weight increase (carbonation) was reached at about the 20 minute CO₂ gas flow time. The reaction was continued for a total of 60 minutes, however. The samples were taken from the furnace after natural cooling, powdered, and the CaCO₃ content determined by ignition loss and the calcimeter method. The data obtained are presented in Table 1. /24

There is a temporary initial increase in CO₂ adsorption at 800°C, although if the CO₂ input conditions are made slightly less favorable, or the CO₂ pressure drops, dissociation again takes place and a fixed level of CO₂ adsorption is not maintained.

Since the decomposition of CaCO₃ takes

place in 10 minutes at 800°C, this temperature level is inappropriate for maintaining adsorption reaction. Maximum CO₂ adsorption occurred at 600°C-700°C. However, the adsorption rate was highest at 600°C. Since this was also the lower of the two temperatures, all of the subsequent adsorption experiments were performed at 600°C. Initial adsorption was higher at 500°C than had been the

Reaction Temp.	Ignition loss	Per Ignition loss	Based on Calcimeter
700	34.30	77.85	76.40
600			77.60
500			
400			
300			
200	3.93	8.92	

Table 1

RELATIONSHIP BETWEEN REACTION
TEMPERATURE AND CARBONATION

case at 600 and 700°C. However, later adsorption was somewhat less than at the other two temperature ranges. This tendency became more and more evident at the 400 and 300°C levels, adsorption becoming respectively 60% and 45% and dropping to 10% or less at the 200°C level.

In the low temperature atmospheres, adsorption was generally completed in five minutes. A comparable state was attained at the 500°C level in 10 minutes, at the 600°C level in 15 minutes, and at the 700°C level in 20 minutes. This, and the fact that the reaction progressed very little beyond these points, is probably attributable to the fact that even in such highly porous, soft calcined quicklime as this, the surface pores become completely stopped up by the swelling which accompanies CO₂ adsorption, thus completely blocking the further penetration of the CO₂ and resulting in an arrested reaction in a very short period of time.

3. Adsorption of Unglazed Quicklime at Various Temperatures

The optimum adsorption range for the test material in granular form was 500-700°C. 600°C was selected within this range as being the optimum condition for the study of CO₂ adsorption by granular quicklime.

We have previously reported on the nature of quicklime crystal growth when the calcining temperatures were varied. Crystals increased in size as calcining moved from soft calcining to hard calcining and the activity of the quicklime progressively dropped. The following experiments were performed to see whether this change could be confirmed in the adsorption reaction and with the thought that, if such a reaction demonstrated numerically accurate values, such values could profitably be used in the preparation of the calcining records written in this plant. Limestone particles, 30-40 mm in size, were calcined for three hours in an elema electric furnace in which the temperature was raised at a rate of 60°C/min to 930; 1,000; 1,200; and 1,300°C. Nearly regular cubes of 9-10 mm size were cut for use as test samples. After the size of these samples had been accurately measured with a comparator, the samples were placed in the dish of a thermal scale and held at 600°C while CO₂ was passed over them at a rate of 0.3-0.5 l/min. The level of carbonation was determined by measuring the swelling or shrinking of the test samples. The rate of the weight increase resulting from the adsorption of CO₂ was as is shown in Figure 3. However, there was absolutely no apparent swelling or shrinking of the samples as a result of CO₂ adsorption. Further, the CO₂ exposure conditions, and the results of measurements of the test samples 30 minutes later, are given in Table 2. The CO₂ adsorption rate decreased progressively as the type of sample changed from the soft calcined material such as the 930°C calcined quicklime to the harder calcined products. The drop in adsorption was particularly dramatic at 1,100°C. This change is very closely related to the nature of crystal formation in quicklime. It is also thought that the reason for the increasing difference between the internal and external CO₂ adsorption rates which grows greater as the material hardens with calcination is attributable to the shrinking, melting, and fusing of the crystals, and the closing of the gaps between

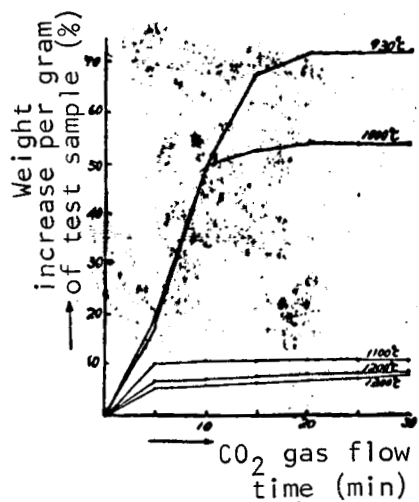


Fig. 3
Calcination Temperature and CO_2
Absorption Velocity in
Unglazed Quicklime

930, 1000, 1100, and 1200°C and CO_2 was brought in contact under exactly the

same conditions as those applied for the unglazed quicklime. The data obtained are given in Figure 4 and Table 3.

the crystals by the melting of impurities contained within the material. These changes obstruct the penetration of CO_2 into the quicklime as does the loss of inter-crystal spaces on the surface of the material as a result of the adsorption of the gas into a very few pores which are present there. This is equivalent to what happens when water is poured over lumps of unglazed quicklime, when it runs right off the surface of the lime and does not, even momentarily, penetrate into the material.

4. Absorption of Sodium Chloride Calcinated Quicklime with Varied Calcined Temperatures

0.1% of table salt was added to limestone and observations like those described above were made of the crystal structure. Limestone was calcined at

Quicklime calcining temperatures	CO_2 temperatures	CO_2 pressure	Volume of CO_2	Interior	Exterior	Difference	Average	Swelling or Shrinkage
930	20	13	13.5	79.3	79.4	0.1	79.35	0
	19.5	13	13.0	77.5	78.5	1.0	78.0	0
1000	26	13	12.6	62.0	66.6	4.6	64.3	0
	19	13	12.5	65.7	66.8	1.1	66.25	0
1100	25	13	11.5	27.2	27.2	0	21.5	0
	18	13	11.5	11.5	21.5	10.0	16.5	0
1200	26	13	12.0	12.0	27.5	15.5	19.75	0
	20.5	13	13.5	12.0	27.5	15.5	19.75	0
1300	25	13	13.2	11.0	17.5	6.5	14.25	0
	10	13	12.0	11.0	17.5	6.5	13.9	0

Table 2
CARBONATION LEVELS OF UNGLAZED QUICKLIME
CALCINED AT VARIOUS TEMPERATURES

Quicklime Calcining Temperatures (°C)	CO ₂ temperatures (°C)	CO ₂ pressure (mmHg)	Volume of CO ₂ (cc)	In the center	At the outside	Difference	Average	Shrinking and swelling (mm)
930	20	12	13	56.0	51.7	-4.3	50.4	0
1000	19	13	14	36.8	42.2	5.4	39.5	0
1100	19	13	13	16.7	13.4	-3.3	15.1	0
1200	20	13	13.5	0.6	0.8	0.2	1.0	0
Current man. product	20	13	14				4.9	0

Table 3.
CARBONATION OF SODIUM CHLORIDE CALCINED QUICKLIME
WHEN CALCINING TEMPERATURES ARE VARIED

The outstanding feature of sodium chloride calcined lime as compared to unglazed quicklime, even when both are calcined under the same conditions, is the dramatically lower CO₂ adsorption rate of the former. Further, the sodium chloride calcined quicklime samples also show a completely opposite trend in the differences between internal and external CO₂ adsorption in the test samples.

In contrast to the clear results of microscopic examination, described in Paragraph 2 above, in which there were considerable differences in the size of the CaO crystals formed in the unglazed limestone which had been calcined at temperatures of 900°C and 1000°C, crystal formation was extensive in the sodium chloride calcined lime even at low calcining temperatures. Crystals which were comparable in size to those formed in the unglazed lime calcined lime at 1000°C and 1100° were formed in the sodium chloride calcined lime at 900°C. For this reason, the product calcined at 930°C would probably show an adsorption rate of about 50%

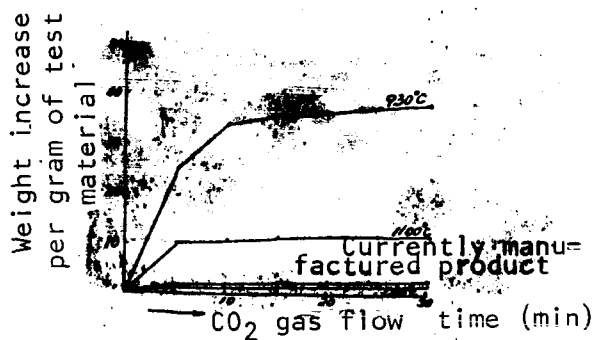


Fig. 4

CO₂ Absorption Rate and Calcining
Temperatures of Sodium Chloride
Calcined Quicklime

When consideration is given to the heating history of normal quicklime in lump form (particularly when calcined at low temperatures), it is apparent that the inside of the lump is calcined at lower temperatures than the outside, thus making the internal portions more active. When simple crystals are regularly distributed, as they are in the sodium chloride calcined lime, the spaces between the crystals are not usually blocked and the material is highly porous. As they are, thus, no obstructions to the permeation of CO₂ into the lump, it may be positively concluded that CO₂ adsorption proceeds faster internally than it does on the interior.

On the other hand, when observations were made of the adsorption of limestone calcined at 1200°C, it was found that 14% of the unglazed limestone changed to CaCO_3 while CaCO_3 formation barely reached 1% in the case of the sodium chloride calcined quicklime. It goes without saying that the crystals were larger in the latter; however, it is believed that the space between the crystals was incomparably lower in the case of the latter, owing to the fusion of the crystals and the fusion of the impurities. It was felt, however, that this great difference could not be solely attributable to differences in the adsorption reaction (differences in activity).

We would like to conduct further detailed experiments into the basic causes for the reduction in the activity of sodium chloride calcined quicklime to determine whether or not the causes are associated only with changes in the crystal structure or whether there are other chemical causes associated with this. There may be, for example, a formation of the so-called salt glaze on the surface of the CaO crystals, or it may be that there is what may be called the inevitable presence of residual chlorine in some form or other in sodium chloride calcined quicklime or perhaps, residual chlorine in the form of Cl^- .

5. Conclusions

When quicklime is brought into contact with dry CO_2 at normal atmospheric pressure and at temperatures of 500-700°C, the CO_2 combines with the CaO directly to form CaCO_3 . It is found, when the CO_2 reaction temperature was held at 600°C, and the quicklime calcining conditions (unglazed, sodium chloride calcined, calcining temperatures) were changed, that a higher volume of CO_2 was adsorbed by the samples which had been calcined at low temperatures. /26 It was found that porosity was reduced in the so-called glazed quicklime and that these samples adsorbed only a small volume of CO_2 . It was particularly apparent that virtually no adsorption took place in sodium chloride calcined quicklime which had been calcined at 1200°C. It is believed that this is an exception to the crystal formation process that takes place during the decarbonation of quicklime. It was found that the adsorption rates in sodium chloride calcined quicklime were lower than those in unglazed quicklime. The preponderant influence of calcining temperature was demonstrated by the accelerated formation of CaO crystals. The positive benefit of the presence of sodium chloride during calcination was clearly demonstrated by the data concerning internal and external adsorption rates in quicklime. It is not believed, however, that all of these effects are attributable solely to the size of the crystals.

In any event, CaO adsorption of CO_2 provides a means by which the chemical activity of CaO may be measured. It is believed that it can be positively asserted that experimental methodology need not be limited to the past method of determining activity on the basis of hydration. We would like to conduct a series of studies on this question.

On the completion of this report, we would like to extend our thanks to Professor Haru for his guidance in the preparation of this material.

REFERENCES

1. Cunningham, W. A., Ind. Eng. Chem, 43, pp. 635-8, 1951.
2. Ohno, Fujiyama, Report at the 14th Academic Lecture Meeting of this Society (Nagoya, November, 1956).

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